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SPECIFICATION

1. TITLE OF THE INVENTION

Antimicrobial Material

2. CLAIM

(1) An antimicrobial material of which the principal component is a polymeric substance that contains sulfone groups and antimicrobial metal ions that are ionically bonded with these sulfone groups.

3. DETAILED DESCRIPTION OF THE INVENTION

This invention relates to an antimicrobial material in which antimicrobial metal ions are ionically bonded to a polymeric substance.

It has long been known that silver ions, copper ions and zinc ions exhibit antimicrobial properties. These antimicrobial metal ions, for example, silver nitrate [sic], are widely used in various fields as antimicrobial agents or disinfectants in the form of salts. However, although these antimicrobial agents have strong antimicrobial activity, they are difficult to handle in the solution state and their uses are limited.

This invention provides a slow-release antimicrobial material in which these antimicrobial ions react with polymeric substances having functional groups and in which the antimicrobial ions are immobilized by the above described functional groups, by which means their use is made possible in such independent states as solutions, emulsions, suspensions, pastes, powders, particles, sheets and films or in states in which they are carried on such carriers as woven cloth and plastic films. As a result, their uses are expanded and they are of superior long-term durability.

Specifically, this invention relates to an antimicrobial material of which the principal component is a polymeric substance that contains sulfone groups and antimicrobial metal ions that are ionically bonded with these sulfone groups.

Such antimicrobial materials can generally be obtained by copolymerizing one or more monomers or polymers that contain sulfone groups or by copolymerizing these monomers with one or more other copolymerizable monomers, bringing the polymeric substances obtained into contact with antimicrobial metal ions and then washing the excess antimicrobial metal ions that are used and drying.

The above described monomers that contain sulfone groups can include styrene sulfonic acid, allyl sulfonic acid, sulfopropyl acrylate, sulfopropyl methacrylate, 3-chloro-4-vinylbenzenesulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid, 2-acryloyloxybenzene sulfonic acid, 2-acryloyloxynaphthalene-2-sulfonic acid, 2-methacryloyloxynaphthalene-2-sulfonic acid, 2-hydroxy-3-sulfopropylmethacrylate and potassium, sodium, ammonium salts thereof.

The above-described monomers that contain sulfone groups and copolymerizable monomers can be selected from a broad range depending on the use of the antimicrobial material. To cite specific examples, they are ethylene, propylene, vinyl chloride, pyridene chloride, vinyl acetate, acrylic acid esters, methacrylic acid esters, styrene and derivatives thereof, allylates such as allyl propyl ether, vinyl ether acrylonitrile and methacrylonitrile.

These monomers may be polymerized by ordinary known methods such as emulsion polymerization, solution polymerization and block polymerization. Emulsion polymerization is particularly desirable because the sulfone groups are distributed in large numbers on the particle surfaces, for which reason there is the advantage that the reaction with the metal ions is performed advantageously.

The antimicrobial metal ions that are used in this invention include silver ions, copper ions and zinc ions. Of these, the use of silver ions are particularly desirable because they have superior antimicrobial activity.

The second method whereby the antimicrobial materials of this invention are obtained is a method in which the above-described monomers that contain sulfone groups are brought into contact with the antimicrobial metal ions and the monomers in which the sulfone groups and the metal ions are bonded by ionic bonds are polymerized or copolymerized in the same way as in the above-described first method.

The third method is a method in which oligomers of a degree of polymerization of 5 to 100 are formed from monomers that contain sulfone groups, after which the antimicrobial metal ions are introduced. They are crosslinked by various crosslinking agents (for example, polyisocyanate compounds, methylolated melamine compounds, peroxides, azylidine compounds) and polymerized.

Further, another method that may be used is a method in which porous coagulates, films, fibers and other molded products are manufactured in accordance with ordinary methods from polymers or copolymers obtained by polymerizing or copolymerizing monomers containing sulfone groups in the same way as described above, after which they are brought into contact with antimicrobial metal ions.

In addition, a method can also be used in which monomers that contain sulfone groups are not manufactured and polymers that do not contain sulfone groups such as styrene polymers are manufactured, and concentrated sulfuric acid or chlorosulfonic acid are reacted with them, with sulfone groups being introduced, after which they are brought into contact with antimicrobial metal ions.

The antimicrobial materials of this invention may be manufactured by any of the above-described methods, and, in addition, various additives may be compounded with these materials at any desired stage up to making them into molded products such as films, depending on the objectives of use.

In order to sufficiently manifest the effect of this invention, the sulfone content and the antimicrobial metal ion content of the antimicrobial material should be a sulfone group content of 0.008 to 2.4 milliequivalents/g of polymer, and, preferably 0.08 to 0.8 milliequivalents/g of polymer, and the antimicrobial ion content should be 0.0009 to 0.9 millimol/g of polymer, and, preferably, 0.0045 to 0.45 millimol/g of polymer.

Next, in order to indicate how superior the antimicrobial materials of this invention are, we shall present a detailed description of the results of the tests indicated below in which antimicrobial films obtained in Working Example 1 to be described subsequently were evaluated.

I. EVALUATION OF ANTIMICROBIAL PROPERTIES: ANTIMICROBIAL ACTIVITY TESTS BY THE DISK METHOD

Test microorganisms: Bacillus subtilis

Staphylococcus aureus

Escherichia coli

Pseudomonas aeruginosa

Candida albicans
Aspergillus niger
Chaetomium glabosum
Cladosporium resinae
Penicillium citrinum

Trichoderma sp.

Of the above described microorganisms, the bacteria were dispersed in quantities of 10^5 to 10^6 bacteria in meat extract agar culture medium and plates were made. The test film was placed on them and they

were cultured overnight at 37°C, after which observations were made of whether zones of inhibition were formed.

On the other hand, for the fungi, potato-sucrose agar culture medium was used, spores were dispersed in a quantity of approximately 10⁵ and plates were made. The test film was placed on them and they were cultured for one week at 30°C, after which observations were made of whether zones of inhibition were formed.

The results of the above described tests are shown in Table 1.

TABLE 1

Test Microorganism	Antimicrobial Activity			
Bacillus subtilis	0			
Staphylococcus aureus	О			
Escherichia coli	О			
Pseudomonas aeruginosa	О			
Candida albicans	O			
Aspergillus niger	О			
Chaetomomium glabosum	О			
Cladosporium resinae	О			
Penicillium citrinium	О			
Trichoderma sp.	О			

O: Zone of inhibition was formed

II. DEATH RATES OF MICROORGANISMS ON FILM

Amounts of $0.1 \text{ ml} (10^4 \sim 10^5 \text{ microorganisms})$ of a spore suspension (0.005% sodium dodecylbenzene sulfonate) of Aspergillus flavus were placed on each film and the test materials were stored at 30°C . After a fixed time, they were sampled, diluted, dispersed in Sabouraud culture medium and made into plates. They were cultured for 24 hours at 30°C , after which the numbers of surviving organisms was determined and the death rates were found. When this was done, it was found that 99% of the organisms had died after 24 hours.

III. DURABILITY OF ANTIMICROBIAL ACTIVITY

Cladosporium resinae was used as the test microorganism, a 5 cm \times 5 cm test film was washed repeatedly with 5 liters of water and evaluations were made of durability on the basis of the number of

washings up to loss of antimicrobial activity. The results are shown in Table 2.

For the purpose of comparison, tests were performed in the same way as for the antimicrobial film of a comparative example described below in which the antimicrobial metal ions were not immobilized by sulfone groups but were simply blended. The results are shown in Table 2.

TABLE 2

Washing frequency (times)	0	100	200	560	720
This Example	О	0	О	О	О
Comparative Example	О	×	×	×	×

O: Zone of inhibition formed by disk method

x: Zone of inhibition not formed by disk method

As should be clear from the above-described results, the antimicrobial material of this invention exhibits superior antimicrobial activity against both bacteria and fungi, has a great capacity to kill microorganisms on films and has extremely superior durability of its antimicrobial activity.

The antimicrobial material of this invention which has this effect, as can be understood from what has been described above, can be used in independent states such as the liquid state, emulsions, suspensions, powders, granules, sheets or films, molded products, porous coagulates (including porous films) and fibers and it can also be used in states in which it is combined with carriers such as nonwoven fabrics, foamed sheets, paper, plastic films and inorganic plates. It can be applied to a broad range of uses such as, for example various coating compositions such as paints for ships and wall paint for buildings, filtration materials, ion exchange materials, dialysis membranes, additives for slime prevention such as pulp slurries, packaging materials, air filters, wallpaper, bed covers for hospital use, sheets, sterile clothing or linings for cabinets, clothes closets and eating utensil shelves.

Next, we shall present a further detailed explanation of this invention by means of working examples. Parts and % in the following working examples signify parts by weight and weight %, respectively.

WORKING EXAMPLE 1

100 parts of a monomer mixture comprised of 45% methyl methacrylate, 50% ethyl acrylate and 5% sulfopropyl methacrylate were dispersed in 150 parts of an aqueous solution containing 0.5% of ammonium

persulfate and 5% of emulsifying agent (Neugen EA 160, manufactured by Daichi Pharmaceuticals K.K [= Ltd.]), polymerization was begun at 70°C as the emulsion was stirred in a nitrogen atmosphere and was maintained for 5 hours at approximately 75°C, with polymerization being completed. Next, some of the coagulated matter in the emulsion was removed by filtration and an emulsion of an essentially homogeneous particle size was obtained.

There was 40% of nonvolatile solid matter in this emulsion and its average particles size was $0.10~\mu$. This emulsion was spread on a glass plate, after which it was immediately immersed for approximately 5 minutes in a medium (water: methyl ethyl ketone = 7:3) in which 5% of hydrochloric acid was dissolved and a porous aggregate in which some of the particles were fused was formed. This aggregate was immersed in purified water, the above-described medium that was absorbed was replaced with water until a state of equilibrium was reached, after which the aggregate was pealed from the glass plate, washed with water and dried.

The porous aggregate that was obtained was immersed for 20 minutes in a 5% aqueous solution of AgNO₃, after which it was thoroughly washed with water and dried, by which means an antimicrobial porous film in which Ag⁺ ions were immobilized in sulfone groups was obtained.

The results of tests of the antimicrobial activity of this film have already been described. In order to make a separate evaluation of durability, it was immersed in boiling water and a study was made by the disk method of the time until antimicrobial activity was not found. As the result, it was six months or longer. The test bacterium that was used at this time was Escherichia coli. This type of porous film can be used in unaltered form or reinforced by nonwoven fabric as a filtration material for water containing microorganisms or as an air filter.

WORKING EXAMPLE 2

A monomer mixture comprised of 50% styrene, 40% ethyl acrylate and 10% sodium 2-acrylamido-2-methylpropane sulfonate was subjected to emulsion polymerization by the same method as in Working Example 1 and an emulsion of an average particle diameter of 0.09 μ and 45% of nonvolatile solid components was obtained.

This emulsion was spread on a polyester film and was dried for 3 minutes at 120°C, with a homogeneous film being obtained. The film that was obtained was

immersed for 30 minutes in a 5% aqueous solution of AgNO₃, after which it was thoroughly washed with water and dried and an antimicrobial film having Ag⁺ ions immobilized in sulfone groups was obtained.

WORKING EXAMPLE 3

A monomer mixture comprised of 55% methyl methacrylate, 37% butyl acrylate, 5% styrene sulfonic acid and 3% styrene sulfonic acid – silver salt monomer was subjected to emulsion polymerization by the same method as in Working Example 1 and an emulsion of an average particle diameter of 0.11 μ and 45% of nonvolatile solid components was obtained.

In order to perform evaluations of the antimicrobial properties, durability and other evaluations of this emulsion, it was spread on a polyester film and dried for 3 minutes at 80°C, with a homogeneous film being obtained. When the various evaluation tests of the film that was obtained were performed by the same methods as in Working Example 1, the same excellent results as in Working Example 1 were obtained. The antimicrobial synthetic resin emulsion that was obtained in Working Example 3 can be used as a composition for various types of coatings such as paints for ships and wall paints for buildings, and, in addition, if it is made into a film, can be widely used as wallpaper and bed covers, and, when molded into fibers, in antimicrobial clothing.

WORKING EXAMPLE 4

100 parts of a monomer mixture comprised of 30% methyl methacrylate, 60% ethyl acrylate and 10% glycidyl methacrylate was dispersed in 130 parts of an aqueous solution containing 5% of emulsifying agent (Neugen EA 160, manufactured by Daichi Pharmaceuticals K.K [= Ltd.]), polymerization was performed at 40°C as the emulsion was stirred in a nitrogen atmosphere using hydrogen persulfate – sodium ascorbate as the initiator. After polymerization was completed, some of the coagulated matter in the emulsion was removed by filtration and an emulsion of an essentially homogeneous particle size was obtained.

There was 46% of nonvolatile solid matter in this emulsion and its average particle size was 0.15 μ . This emulsion was made into a porous aggregate by the same method as in Working Example 1.

This porous aggregate was immersed in a 5% aqueous solution of sodium hydrogen sulfite in which it was treated for 5 hours at 60°C. It was further reacted for 2 hours at 80°C. By this means, the sulfone groups were introduced into the glycidyl groups. The quantity

of sulfone groups that was introduced was 0.2 milliequivalents/g. This film was thoroughly washed with water, after which it was immersed in a 5% aqueous solution of $AgNO_3$ for 30 minutes. It was then thoroughly washed with water, after which it was dried with an antimicrobial porous film in which Ag^+ ions immobilized in the sulfone groups were obtained.

COMPARATIVE EXAMPLE

A monomer mixture comprised of 50% styrene, 49% ethyl acrylate and 1% divinyl benzene was subjected to emulsion polymerization by the same method as in Working Example 1 and a emulsion of an average particle diameter of 0.22 μ and 44% of nonvolatile solid components was obtained.

4 parts of a 10% aqueous solution of AgNO₃ was added to 100 parts of this emulsion, after which it was spread on a polyester film and dried for 3 minutes at 145°C, with an homogeneous film being obtained.

The antimicrobial agent was merely blended in the film that was obtained. As the result of tests of the durability of the antimicrobial activity of this film, it was found that its antimicrobial activity was comparatively easily lost by water washing.

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